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Microwave assisted patterning of vertically aligned carbon nanotubes onto polymer substrates

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This paper presents a low pressure hot embossing method for transferring patterns of vertically aligned carbon nanotubes into thermoplastic substrates. The procedure utilizes the synthesis of carbon nanotubes in discrete patterns on silicon substrates through the vapor liquid solid growth mechanism. The nanotube pattern and silicon stamp is placed on top of a polycarbonate film and locally heated above the glass transition temperature using microwave processing. The weight of the silicon substrate presses the nanotubes into the polycarbonate, resulting in the complete transfer of vertically aligned patterns. The technique is a rapid processing method, which could be used to integrate aligned nanomaterials with MEMS and flexible electronics that are fabricated on a wide range of thermoplastic polymer materials. © *2006 American Vacuum Society.*
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I. INTRODUCTION

The extraordinary properties of carbon nanotubes have motivated much research on their processing, integration, and applications. Electrical conduction through networks of single wall carbon nanotubes have shown transport mobility close to 270 $cm^2/V\,s$, which is order of magnitudes greater than amorphous silicon and makes them intriguing candidates for organic transistors.[1] In addition, carbon nanotube networks show little degradation in electrical performance under extreme deformation which is attractive for use in flexible macroelectronic devices.[2,3] Applications that could harness these features of carbon nanotubes include transparent flexible electrodes, sensors, nanocomposites for organic electronics, and structures for heat dissipation.[3–8] The successful integration of carbon nanotubes into devices and systems that could exploit their properties requires manufacturing technologies that can disperse or pattern them into target systems and materials. Carbon nanotubes are most often grown using chemical vapor deposition (CVD), which requires temperatures in the range 700–900 °C.[9] Typical substrate materials for carbon nanotube growth include silicon and sapphire, as these materials can withstand these high temperatures. Carbon nanotubes can be made to self-assemble in discrete patterns on these substrates through the vapor liquid solid growth mechanism, through the use of transitional metal catalysts patterned onto these substrates. The high temperatures required for carbon nanotube growth preclude direct synthesis on many materials, including polymer substrates. However, carbon nanotubes patterned on polymer substrates could enable low-cost microelectronic devices. Advances in patterning technologies are, therefore, required to perform this integration.

Several technologies have been developed for dispensing and patterning carbon nanotubes and other semiconductor nanomaterials onto polymer substrates, either by self-assembly or direct printing.[4,10–15] Solution-based printing methods rely on the development of a nanomaterial suspension which is then deposited using spin casting, flow-directed alignment, or electrophoretic trapping. Dry transfer methods have also been developed where the nanomaterials are transferred directly from an intermediate substrate (e.g., PDMS, silicon) to the polymer through microcontact printing or hot embossing.[16] Electric field assisted patterning of nanomaterials has also shown promise for direct patterning on polymer films through the creation of a thin film electret.[10,11] These patterning methods lack the ability to form arrays of nanomaterials aligned vertically relative to the substrate. Vertical alignment of carbon nanotubes are desirable to create features such as high thermal conductivity vias, thermal interface materials, flexible field emitters, and electrical interconnect structures. The transfer of vertically aligned carbon nanotubes in polymer substrates was recently demonstrated by casting a polymer solution around the nanotube arrays.[17,18] While achieving excellent pattern transfer, the nanotubes could be exposed only with a chemical etch that partially removed the polymer. As this approach is only compatible with castable polymers, additional work is required to

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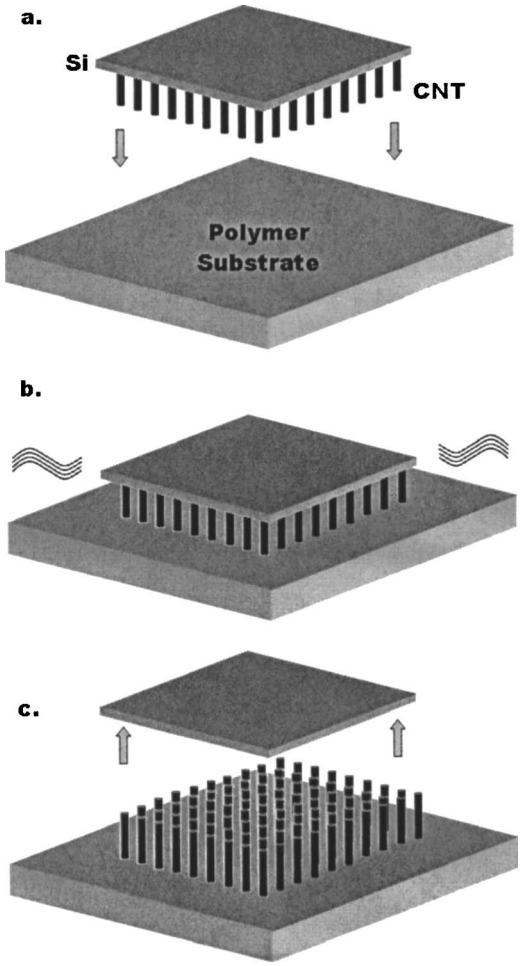

FIG. 1. Depiction of the microwave assisted printing of vertical carbon nanotubes. First, (a) the nanotubes are grown on a silicon substrate which is placed faced down on a thermoplastic polymer sheet. Next, (b) microwave energy is applied to locally heat the carbon nanotubes while the silicon substrate is used to apply pressure to the nanotube array for embossing. Finally, (c) the silicon substrate is manually removed, leaving behind the nanotube pattern in the polymer substrate.

develop methods of patterning vertical arrays of carbon nanotubes with a wider array of polymer materials.

This paper presents a method for printing vertical arrays of carbon nanotubes onto thermoplastic polymers using a low pressure hot embossing method. In this method, the carbon nanotubes are grown in discrete patterns on a silicon substrate and then transferred into the polymer using microwave assisted heating. The microwave processing induces localized heating of the silicon and carbon nanotubes such that the nanotube-polymer interface exceeds the glass transition temperature of the polymer while pressure is applied by the weight of the silicon substrate. The process results in a rapid transfer of well-aligned carbon nanotube patterns and is compatible with a wide range of thermoplastic materials.

II. FABRICATION PROCEDURE

Figure 1 shows the process in which carbon nanotubes were transferred into a commercially available polycarbonate film. Vertically aligned carbon nanotube arrays were grown on a silicon substrate by chemical vapor deposition. First, a 200 nm thermal oxide layer was grown on a 525 μm thick silicon substrate as a catalyst support. To promote the self-assembly of carbon nanotube arrays, a 5 nm iron thin film was patterned on the oxidized surface using standard photolithography and lift off techniques. Patterns consisted of arrays of circles that were 10 μm in diameter and squares which were 750 μm on a side. The sample was placed in a quartz tube furnace and heated to 740 °C for 10 min under 1000 sccm of argon flow to promote the break up of the Fe catalyst into nanoparticle nucleation sites. Carbon nanotubes were grown using a mixture of methane, acetylene and hydrogen at flowrates of 1000, 100, and 500 sccm, respectively, for 15 min. Inspection of the carbon nanotubes showed excellent vertical alignment with an average diameter of 20 nm and a height of 50 μm. Micro-Raman spectroscopy measurements indicated a graphitic to defect intensity ratio greater than 1.5. No radial breathing mode was observed, indicating that the tubes were multiwalled. By varying the synthesis time, gas flow rates and substituting ethylene for acetylene, the vertically aligned carbon nanotube height could be easily varied from 2 to 200 μm.

The silicon master with the aligned CNT patterns was then placed on a 500 μm thick polycarbonate film with the nanotubes facing the polymer. Care was taken to ensure that very little translation or shifting of the silicon substrate occurred in order to prevent shearing of the nanotube patterns. Avoiding the shearing of the nanotube patterns was important for printing vertically aligned tubes since the weak SiO_2-supported Fe catalyst interface promoted easy removal of the tubes with applied force. Thus, distortions from shearing would result in tubes being removed from the stamp prior to printing. It would be possible to use a multilayer catalyst structure including films such as Ti and Al to promote greater adhesion, if desired, which would allow shearing to be used to print patterns at an angle. In the current approach as depicted in Fig. 1, the polycarbonate/nanotube/silicon structure resulted in the weight of the silicon substrate being supported by the nanotube arrays which provided the pressure during the embossing process.

The sandwiched structure of silicon, CNTs and polycarbonate was then placed inside a Lambda Technology model Microcure 2100 variable frequency microwave (VFM) to locally heat the carbon nanotube pattern. The microwaves were emitted by a CPI brand rack mounted generator. In this process, the conductive silicon and carbon nanotube features coupled with the microwave energy which caused them to heat while the polycarbonate remained at room temperature. As a result of the low thermal conductivity of the polycarbonate film, highly localized heating occurred at the nanotube-polymer interface. The microwave processing was operated under temperature control where the microwave source was pulsed in order to heat the sample to a desired temperature. In this arrangement, a fiber optic-coupled infrared sensor monitored the backside of the silicon chip; monitoring the temperature of the nanotubes directly was not possible. For temperature measurements, an emissivity of 0.75

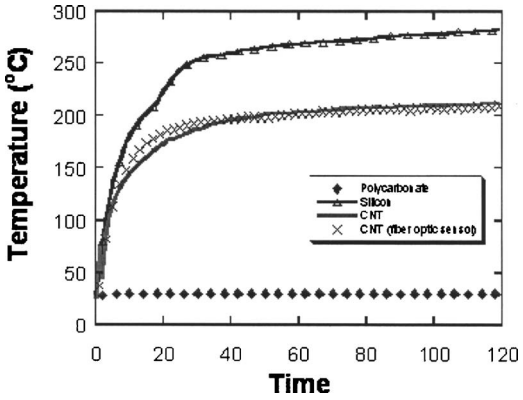

FIG. 2. Graph showing the heating of the polycarbonate, silicon, and carbon nanotube materials used in the microwave assisted printing. Data reveal that the silicon substrate is the most susceptible to heating when exposed to 60 W of microwave energy at 6.425±1.15 GHz. Based on this data, the silicon substrate is used as an indicator of the carbon nanotube temperature for the printing structure depicted in Fig. 1.

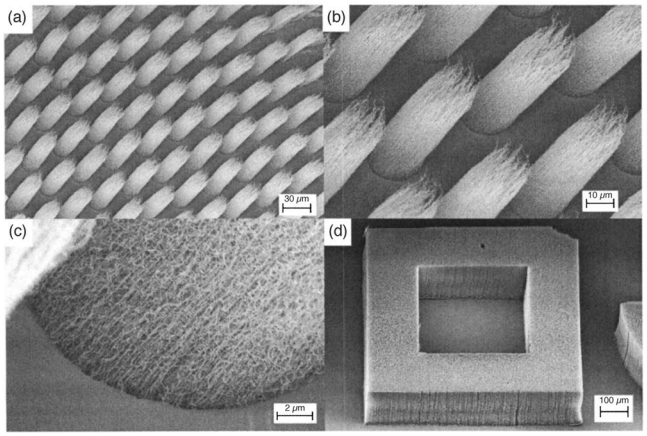

FIG. 3. Results of the microwave assisted transfer of vertical multiwall carbon nanotube arrays into polycarbonate films analyzed by scanning electron microscopy. Image A shows an array of 10 μm diameter carbon nanotube pillars. Image B shows details of the tearing effect at the top of the CNT pillars. Image C shows details of a single pillar buried in the polycarbonate substrate. Image D shows the transfer of a square array of carbon nanotubes. A weak interface with the SiO_2 substrate resulted in the clean transfer of the CNT array with a uniform height.

was used for the rough silicon surface which correlated well with calibrations on a Quantum Focus Infrascope IR microscope system.

To determine if monitoring the backside of the silicon substrate was sufficient for estimating the nanotube temperature, separate microwave heating experiments for a polycarbonate, silicon, and carbon nanotube sample were performed. First, an IR sensor was focused on a polycarbonate film which was exposed to 60 W of microwave energy for 2 min. Virtually no heating of the polycarbonate was observed, as seen in Fig. 2. Next, a blanket film of carbon nanotubes followed by a bare silicon sample were also exposed for two minutes and monitored by the IR sensor. Figure 2 shows that both the carbon nanotubes and silicon sample were subject to heating, with the silicon obtaining a higher temperature in both cases. An additional fiber optic based IR sensor was also used during the silicon heating experiments which agreed well with the remote IR sensor (Fig. 2). These data suggest that during the processing of the structure in Fig. 1, the silicon substrate obtains the highest temperature of any layer during microwave exposure. Since the carbon nanotubes also have a high thermal conductivity and low thermal mass, the nanotubes are expected to exhibit very little temperature drop between the surface of the silicon and the tip of the nanotubes. The backside silicon temperature is thus expected to be a good estimate of the carbon nanotube tip temperature.

Using the variable frequency microwave excitation, the backside temperature of the silicon was raised to 145 °C at a rate of 2 °C/s and held for 4 min to allow for pattern transfer. The emitted center frequency was 6.425 GHz and varied over a bandwidth of 1.15 GHz every 0.1 s. After microwave exposure, the sample was allowed to cool back to room temperature before being removed from the enclosure. The top side silicon was then removed from the assembly by tweezers. Due to the local melting and embossing of the nanotubes in the polymer substrate, the nanotube patterns were easily transferred from the silicon substrate with the weak $Fe-SiO_2$ interface.

III. EXPERIMENTAL RESULTS AND CONCLUSIONS

Figure 3 shows the transfer of cylindrical carbon nanotube towers and square patterns. From the scanning electron microscopy images, it is clear that excellent vertical alignment of the features is maintained from this process. A close up image of the device shows that the tubes are embedded in the polymer layer with little distortion of the polymer around the nanotube towers as a result of the localized heating of the polymer around the nanotubes. In the case of the nanotube towers, the carbon nanotubes appeared "torn" at the top surface. An inspection of the silicon stamp after the microwave transfer process revealed a number of carbon nanotubes still adhered to the silicon surface. Subsequent trials resulted in a very clean transfer from the silicon stamp as shown with the square feature in Fig. 2. While it is not clear the reason for the adhesion between the nanotubes and silicon stamp in the first transfer, this result suggests that altering the adhesion of the catalyst layer to the Si can be used to manipulate the exposed surface after the transfer. In the case of the torn nanotubes, less of the Fe catalyst is transferred with the nanotubes, which may be beneficial in applications where metal is not desired, for example, carbon nanotube templates for biological cell growth. Transfers with the weak interface results in features with a very uniform and flat tops which are desirable for creating field emission devices on flexible substrates where a counter electrode is placed at a uniform spacing from the CNTs.

The microwave assisted transfer method creates a locally

heated embossing stamp with low thermal mass which has the ability to rapidly heat and cool. This is in direct contrast to imprint lithography tools where large platens must be heated and cooled with large thermal time constants. Thus, the microwave processing provides a rapid method for nanomaterial transfer into thermoplastic polymers. The use of a silicon substrate enables the localized absorption and heating of the nanomaterials, even if the microwave energy absorptivity of the nanomaterial is low. The absorption of the microwave energy by the nanotubes is dependent on nanotube diameter, impurity concentration, and nanotube properties. While our nanotubes were metallic and approximately 20 nm in diameter, previous research suggests that small diameter single wall nanotubes are highly susceptible to microwave energy absorption and may even heat enough to thermally decompose.[19–22] Such decomposition was not seen from our exposure of multiwall carbon nanotubes as evident by SEM and Raman spectroscopy.

The patterning of vertically aligned carbon nanotubes is technologically important with applications in a wide range of technologies. This includes field emission displays, high thermal conductivity vias and interconnects, electrodes for flexible organic electronics, and superhydrophobic self-cleaning surfaces. Results of experiments of water droplets on the pattern in Fig. 3 showed a contact angle measurement of 168°. Optimization of nanotube pattern is expected to push this value above 170°. While the technique presented here utilized carbon nanotubes in polycarbonate, the methodology can be extended to other semiconductor nanomaterials which can be grown vertically on silicon substrates or substrates which are susceptible to microwave heating. Such nanomaterials include important wide bandgap semiconductors such as ZnO and GaN which are used in optoelectronic applications. At present, the method provides a quick and reliable method of vertical carbon nanotube printing which can be overlayed and integrated with polymer MEMS and flexible electronic devices which is not possible with other printing methods. In addition, the technology extends the integration of these materials with a wide range of thermoplastic polymers which are technologically important.

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[1]Y. Zhou, A. Gaur, S.-H. Hur, C. Kocabas, M. A. Meitl, M. Shim, and J. A. Rogers, Nano Lett. **4**, 2031 (2004).
[2]S.-H. Hur, O. O. Park, and J. A. Rogers, Appl. Phys. Lett. **86**, 243502 (2005).
[3]W. Zhuangchun, C. Zhihong, D. Xu, J. M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J. R. Reynolds, D. B. Tanner, A. F. Hebard, and A. G. Rinzler, Science **305**, 1273-6 (2004).
[4]C. K. M. Fung, V. T. S. Wong, R. H. M. Chan, and W. J. Li, IEEE Trans. Nanotechnol. **3**, 395 (2004).
[5]A. Du Pasquier, H. E. Unalan, A. Kanwal, S. Miller, and M. Chhowalla, Appl. Phys. Lett. **87**, 203511 (2005).
[6]X. Z. Bo, C. Y. Lee, M. S. Strano, M. Goldfinger, C. Nuckolls, and G. B. Blanchet, Appl. Phys. Lett. **86**, 182102 (2005).
[7]H. Ago, K. Petritsch, M. S. P. Shaffer, A. H. Windle, and R. H. Friend, Adv. Mater. (Weinheim, Ger.) **11**, 1281 (1999).
[8]E. Kymakis and G. A. J. Amaratunga, Appl. Phys. Lett. **80**, 112 (2002).
[9]A. V. Melechko, V. I. Merkulov, T. E. McKnight, M. A. Guillorn, K. L. Klein, D. H. Lowndes, and M. L. Simpson, J. Appl. Phys. **97**, 041301 (2005).
[10]C. R. Barry, N. Z. Lwin, W. Zheng, and H. O. Jacobs, Appl. Phys. Lett. **83**, 5527 (2003).
[11]H. O. Jacobs and G. M. Whitesides, Science **291**, 1763 (2001).
[12]G. Blanchet and J. Rogers, J. Imaging Sci. Technol. **47**, 296 (2003).
[13]G. B. Blanchet, S. Subramoney, R. K. Bailey, G. D. Jaycox, and C. Nuckolls, Appl. Phys. Lett. **85**, 828 (2004).
[14]H. Yu, D. Xiangfeng, W. Qingqiao, and C. M. Lieber, Science **291**, 630 (2001).
[15]W. Dongmok, J. Song, W. Yue, and C. M. Lieber, Nano Lett. **3**, 1255 (2003).
[16]A. C. Allen, E. Sunden, A. Cannon, S. Graham, and W. King,Appl. Phys. Lett. **88**, 083112 (2006).
[17]Y. J. Jung, S. Kar, S. Talapatra, C. Soldano, G. Viswanathan, X. Li, Y. Zhaoling, F. S. Ou, A. Avadhanula, R. Vajtai, S. Curran, O. Nalamasu, and P. M. Ajayan, Nano Lett. **6**, 413 (2006).
[18]N. R. Raravikar, L. S. Schadler, A. Vijayaraghavan, Y. Zhao, B. Wei, and P. M. Ajayan, Chem. Mater. **17**, 974 (2005).
[19]R. C. Che, C. Y. Zhi, C. Y. Liang, and X. G. Zhou, Appl. Phys. Lett. **88**, 033105 (2006).
[20]J. N. Dahiya, R. Athinarayanan, J. A. Roberts, J. M. Tour, and D. W. Price, Jr., *Microwave Absorption in Liquid Crystals and Carbon Nanotubes* (Ostrava, Czech Republic, 2004).
[21]T. J. Imholt, C. A. Dyke, B. Hasslacher, J. M. Perez, D. W. Price, J. A. Roberts, J. B. Scott, A. Wadhawan, Z. Ye, and J. M. Tour, Chem. Mater. **15**, 3969 (2003).
[22]A. Wadhawan, D. Garrett, and J. M. Perez, Appl. Phys. Lett. **83**, 2683 (2003).